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Facile preparation of high-capacity hydrogen storage metal-organic frameworks: A combination of microwave-assisted solvothermal synthesis and supercritical activation

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ABSTRACT

The $Cu_3(BTC)_2$ Metal—oragnic frameworks (MOFs) are synthesized by four different processes, i.e. solvothermal method (sample 1), microwave-assisted solvothermal method (sample 2), a combination of solvothermal method and supercritical carbon dioxide (Sc-CO_2) activation (sample 3) and a combination of microwave-assisted solvothermal method and Sc-CO_2 activation (sample 4). By comparing the N_2 adsorption isotherms of the four samples, it is found that the sample 4 displays the greatest N_2 uptake. Due to the best performance of sample 4 in N_2 adsorption, we further study H_2 adsorption in the sample 4. Results indicate that the excess and absolute hydrogen uptakes of this material reach 4.12 and 4.49 wt% at $T=77$ K and $P=18$ bar, respectively, which is the largest one among all these reports on $Cu_3(BTC)_2$ for H_2 storage at the same condition. Therefore, it is believed that a combination of the two technologies of microwave-assisted method and supercritical Sc-CO_2 activation provides a new approach for chemical engineers rapidly and efficiently preparing MOFs for high-capacity H_2 storage.

1. Introduction

As a family of highly porous materials, metal-organic framewoks (MOFs) (Furukawa et al., 2007; Lin et al., 2009; Xiang et al., 2009) have become a very hot topic in hydrogen economics (Basic Research Needs for the Hydrogen Economy, 2003), because some MOFs, such as MOF-177 and MOF-5, have shown excellent performance for H_2 storage. Nowadays, MOFs have been commonly synthesized via a solvothermal method, and the solvent occluded in MOFs is extracted by a volatile solvent (Chui et al., 1999; Lin et al., 2009; Xiao et al., 2007). For the solvothermal method, the crystallization time takes nearly 1/2 day to several days in most cases. Recent studies indicated that a microwave-assisted solvothermal method needed a significantly short crystallization time, about several minutes or hours in most cases, in preparing MOFs (Jhung et al., 2007; Ni and Masel, 2006). In addition, loss of solvent in conventional activiation procedures can create a surface tension that drives the pores to collapse, resulting in considerably poor pore performance than those predicted by computational method (Walton and Snurr, 2007). Recently, Hupp et al. (Nelson et al., 2009) sucessfully maximized gas-accessible specific surface area (SSA) of MOFs by a supercritical drying procedure. In the supercritical activation, pore blockage can be avoided dynamically, and there is less collapse of interparticle after removal of solvent (Cooper and Rosseinsky, 2009). In most previous studies, investigators only used one of the above two techniques. Actually, a combination of the two techniques suggests a new direction for the future prepation of MOFs. Therefore, in this work we combine the two techniques to yield a rapid and efficient means to prepare MOFs for gas adsorption application.

In particular, a lot of researchers (Dinca and Long, 2008; Lin et al., 2009; Vitillo et al., 2008) have shown that these MOFs with unsaturated metal centers exhibit a high capacity for H_2 storage, because the open metal sites can participate in the binding of H_2 directly. Therefore, the open metal sites can enhance the van der Waals affinity towards H_2 molecules, resulting in a higher heat of adsorption and an improved H_2 storage capacity. The octahedral crystals $Cu_3(BTC)_2$ is a typical coordination framework with open metal sites and has been widely studied (Krawiec et al., 2006; Panella et al., 2006; Rowsell and Yaghi, 2006; Wong-Foy et al., 2006). Fig. 1 shows the $Cu_3(BTC)_2$ structure assembled by the coordinate bond between Cu ions and tricarboxylate (H_3BTC), which was firstly reported by Williams et al. (Chui et al., 1999) Fig. 1c shows the scheme of formation of an unsaturated copper metal site. The water combined with Cu^{2+} species can be removed during the process of activation without rearrangement of Cu_2-tricarboxylate paddlewheel building clusters and collapse of the frameworks, which yields a coordinative vacancy on Cu^{2+} species. The open

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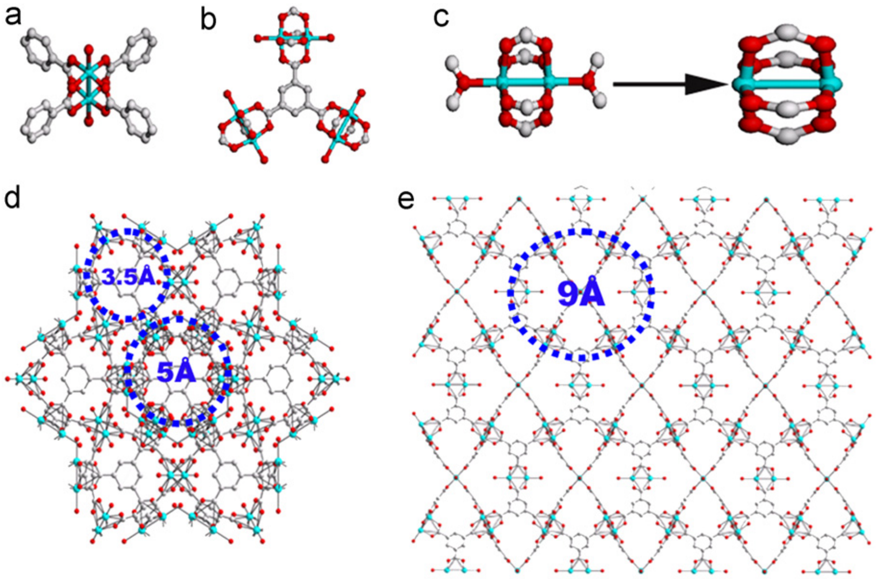

Fig. 1. The 3D structure of $Cu_3(BTC)_2$: (a) The copper secondary building unit (SBU) connected four linkers; (b) the linker connected three copper SBUs; (c) the scheme of formation of unsaturated metal site; (d) structure along the [1 1 1] direction, where tetrahedral-shaped cages of diameter ~5 Å are accessible from the larger pores and the triangular windows are 3.5 Å in diameter; and (e) A 2 × 2 × 2 supercell along the [1 0 1] direction, where the largest pores are ~9 Å in diameter formed by 12 paddle-wheel dinuclear $Cu_2(OOC)_4$ subunits. All atoms are shown as spheres; C: light gray, Cu: blue, O: red, H atoms are omitted except the image in c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

metal site plays a very important role in H_2 storage. Moreover, the low-temperature powder neutron diffraction experiments validated that D_2 primarily binds to the empty axial coordination sites of Cu_2-tricarboxylate paddlewheel building units (Peterson et al., 2006). To further explore the application of MOFs in H_2 storage, here we intent to prepare $Cu_3(BTC)_2$ by different methods mentioned above.

2. Experiment

2.1. Synthetic procedures for $Cu_3(BTC)_2$ with different methods

2.1.1. Solvothermal method (sample 1)

Benzene-1,3,5-tricarboxylic acid (2.5 g, 12 mmol) and copper nitrate hemihexadihydrate (5 g, 21.5 mmol) were sonicated for 15 min in a 125 mL solvent consisting of equal parts of *N*,*N*-dimethylformamide (DMF), ethanol, and deionized water in a 300 mL wide mouth glass jar. The jar was placed in an oven at 85 °C for 20 h. The product was isolated by filtration and rinsing with 3 × 10 mL DMF, and then immersed in $CHCl_3$ for 3 days, during which the activation solvent was decanted and fleshly replenished three times. The product was dried at 200 °C in vacuum to yield sample **1**.

2.1.2. Microwave-assisted solvothermal method (sample 2)

Benzene-1,3,5-tricarboxylic acid (2.5 g, 12 mmol) and copper nitrate hemihexadihydrate (5 g, 21.5 mmol) was sonicated for 15 min in a 125 mL solvent consisting of equal parts of *N*,*N*-dimethylformamide (DMF), ethanol, and deionized water in a 300 mL wide mouth glass jar. The jar was then placed inside household microwave oven (Galanz, PT021TP-6) and heated at 700 W for 4 min, during which the jar was put out from microwave oven for a little while with slight stir every minute to avoid explosion. A blue suspension was formed after the microwave treatment. The product was isolated and then rinsed with 3 × 10 mL DMF. After exchanging with $CHCl_3$ for three days, the product was dried at 200 °C in vacuum to yield sample 2.

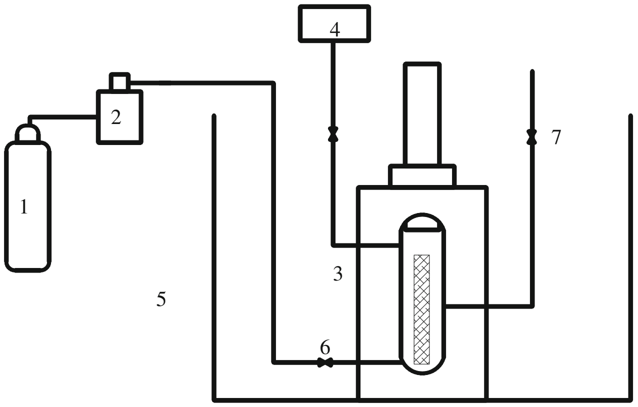

Fig. 2. Schematic diagram of the apparatus: (1) CO_2 cylinder; (2) Computer-controlled metering syringe pump; (3) High-pressure variable volume view cell; (4) Pressure gauge; (5) Constant temperature water bath; (6) Intake valve and (7) Export valve.

2.1.3. Description of supercritical apparatus

As shown in Fig. 2, during the procedures of preparing the sample 3, 4, the ethanol-contained sample was put in the chamber of variable volume view cell. The cell was put in a constant temperature water bath with the temperature of 40 °C. The carbon dioxide was pumped into the chamber by computer-controlled metering syringe pump with the rate of 50–500 $ml\,min^{-1}$. The pressure gauge displays the pressure of the chamber of view cell. The balance of pressure of 15 MPa in chamber was maintained by controlling the export value. The sample was hold in the chamber above the critical point for four hours to yield the activated samples.

2.1.4. Combination of solvothermal synthesis and Sc-CO_2 drying (sample 3)

After following the procedure for sample 1, the isolated powder by filtration was then immersed in absolute ethanol every 24 h for 72 h instead of $CHCl_3$. The ethanol-contained sample was placed inside the high-pressure variable volume view